<Division of Multidisciplinary Chemistry>Molecular Aggregation Analysis

Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

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Scope of Research

We design and synthesize unique electronic materials with sophisticated device applications in mind. These materials have novel solid-state aggregation structures or well-defined interface orientation that promote efficient electrical current flow or enhance device lifetime. Electronic devices based on these new materials are then evaluated using advanced measurement techniques, and the results are used to inform the next direction of the materials chemistry. We call this synergistic approach for achieving our research goals “Needs Inspired Fundamental Science”.

KEYWORDS

Molecular Design and Synthesis
Molecular Aggregation
Functional Materials
Semiconductors
Perovskite Solar Cells

Selected Publications

Lin, H.-A.; Mitoma, N.; Meng, L.; Segawa, Y.; Wakamiya, A.; Itami, K., Hole-Transporting Materials Based on Thiophene-Fused Arenes from Sulfur-Mediated Thienannulations, *Mater. Chem. Front.*, **2,** 275-280 (2018).

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Murdey, R.; Katoh, K.; Yamashita, M.; Sato, N., Thermally Activated Electrical Conductivity of Thin Films of Bis(phthalocyaninato)terbium(III) Double Decker Complex, *Thin Solid Films*, **646,** 17-20 (2018).

Shimogawa, H.; Murata, Y.; Wakamiya, A., NIR-Absorbing Dye Based on BF2-Bridged Azafulvene Dimer as a Strong Electron-Accepting Unit, *Org. Lett.*, **20,** 5135-5138 (2018).

Liu, J.; Ozaki, M.; Yakumaru, S.; Handa, T.; Nishikubo, R.; Kanemitsu, Y.; Saeki, A.; Murata, Y.; Murdey, R.; Wakamiya, A., Lead-Free Solar Cells Based on Tin Halide Perovskite Films with High Coverage and Improved Aggregation, *Angew. Chem. Int. Ed.*, **57,** 13221-13225 (2018).

Yang, D.-T.; Nakamura, T.; He, Z.; Wang, X.; Wakamiya, A.; Peng, T.; Wang, S., Doping Polycyclic Arenes with Nitrogen−Boron−Nitrogen (NBN) Units, *Org. Lett.*, **20,** 6741-6745 (2018).

NIR-Absorbing Dye Using BF_2-Bridged Azafulvene Dimer Unit

Dyes that absorb near infrared (NIR) light have been investigated intensively in the context of a variety of applications, including photovoltaics, photodetectors, heat absorbers, and medical applications. In many applications, the photostability and resistance to oxidation of these NIR dyes are very important. NIR dyes usually have narrow HOMO–LUMO gaps on account of the destabilized HOMO level, and are thus easily oxidized by atmospheric oxygen. A strong electron-accepting unit having low-lying LUMO levels should, therefore, be expected to lead to NIR dyes with improved air- and photo-stability.

We designed and synthesized a twofold BF_2-bridged azafulvene dimer as a strongly electron-accepting building block. As a model D–A–D dye composed of this electron-acceptor unit, compound 1 was synthesized by combined with electron-donor triarylamine units. In cyclic voltammometry in CH_2Cl_2, D–A–D dye showed two reversible reduction waves at $E_{1/2}$ = –0.78 and –0.98 V (vs. Fc/Fc^+) and two reversible oxidation waves at $E_{1/2}$ = +0.21 and +0.54 V. The first reduction potential appears at a substantially more positive potential than those of typical n-type materials such as fullerene C_{60} ($E_{1/2}$ = –0.98 V) or perylene diimide ($E_{1/2}$ = –0.97 V), demonstrating the significant electron-accepting ability of the BF_2-bridged azafulvene dimer building unit.

In the UV/vis/NIR absorption spectra in CH_2Cl_2, D–A–D dye exhibits an intense NIR absorption at λ_{abs} = 922 nm tailing up to λ_{edge} = 1150 nm, reflecting the narrow HOMO–LUMO gap, while relatively little absorption in the visible region (400-700 nm) was observed. This is the ideal photophysical property for a selective NIR absorber. The photostability test in both degassed and non-degassed toluene solution showed that in sharp contrast to a commercially available naphthalocyanine (Napht) NIR dye, the absorption of which (λ_{abs} = 865 nm) diminished to 27% in degassed toluene and to 6% in non-degassed toluene, the absorption of D–A–D dye remained unchanged (97%) even after irradiation for 50 h, clearly demonstrating the high photostability of our D–A–D dye and its resistance to oxidation by atmospheric oxygen.

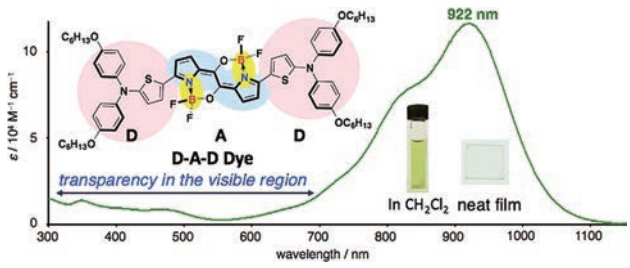

Figure 1. Absorption properties of D–A–D dye containing BF_2-bridged azafulvene dimer as a strong electron-accepting unit.

Fabrication Method for Tin-based Perovskite Films to Give Good PCEs

Metal halide perovskite solar cells (PSCs) have gained tremendous attention in the past few years. However, the toxicity of lead (Pb), commonly used in high efficiency PSCs, remains a serious problem that hampers the wide application of this 'magic' material. Sn-based perovskites replacing Pb^{2+} with tin (II) (Sn^{2+}) are expected to be promising candidates for lead-free perovskites. Unfortunately, power conversion efficiencies (PCEs) obtained from Sn-based PSCs are much lower than that of their Pb counterparts, and the highest PCE achieved for a Sn-based PSC to date is still below 10%. One issue is the fact that rapid oxidation of Sn^{2+} to Sn^{4+} in ambient atmosphere dopes the perovskite layer into high conductivity, resulting in severe electric shorting. Another issue also predominates when the perovskite film is fabricated with uneven thickness or pinholes, a common occurrence for Sn-based PSC. Despite the clear need to improve device performance, only a limited number of groups are investigating Sn-based PSC at present. The difficulty in fabricating high-quality Sn perovskite films is a significant impediment.

Aimed at increasing the power conversion efficiency of lead-free perovskite solar cells, we developed two simple methods to improve tin halide perovskite film structure. First, a hot antisolvent treatment (HAT) was found to increase the film coverage and prevent electric shunting in the photovoltaic device. Second, we discovered that annealing under a low partial pressure of dimethyl sulfoxide vapor increased the average crystallite size. As a result of the combined treatments, the topographical and electrical qualities of the perovskite films can substantively be improved, facilitating the fabrication of Sn-based perovskite solar cell devices with power conversion efficiencies of over 7%.

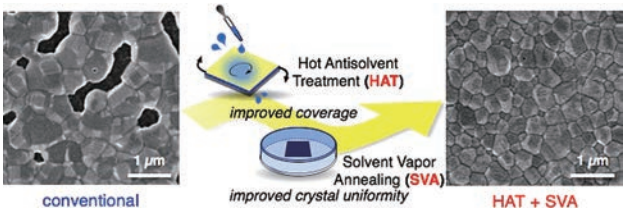

Figure 2. Top view SEM images comparing $FA_{0.75}MA_{0.25}SnI_3$ perovskite films fabricated by the conventional method (left) and with the combined HAT+SVA process (right).